

Synthesis of bio-lubricant from epoxy canola oil using sulfated Ti-SBA-15 catalyst



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ABSTRACT

A green and environmentally friendly one step process for the preparation of bio-lubricant from epoxy canola oil is described in the present investigation. This study deals with simultaneous epoxy ring opening and esterification of epoxy canola oil in the presence of acetic anhydride using novel sulfated Ti-SBA-15(10) catalyst. Optimum reaction conditions were obtained by studying various reaction parameters such as agitation speed, acetic anhydride effect, catalyst loading, and temperature. Sulfated Ti-SBA-15(10) demonstrated 100% conversion of epoxy canola oil to the esterified product (bio-lubricant). Langmuir–Hinshelwood–Hougen–Watson type reaction mechanism was proposed, and the reaction follows a pseudo first order. The energy of activation was found to be 19.0 kcal/mol. The tribological properties of bio-lubricant such as oxidative induction time (56.1 h), cloud point (-3°C), pour point (-9°C), and kinematic viscosity at 100°C was 670 cSt were measured. Prepared bio-lubricant demonstrated the excellent lubricity property by wear scar of $130\ \mu\text{m}$.

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1. Introduction

Lubricants are extensively utilized in industries and automobile sectors for lubricating their machineries and materials. A wide range of lubricant base oils is available in the market, which are derived from mineral oil, synthetic oil, refined oil, and vegetable oil. Among them, lubricants derived from mineral oil are most commonly used although they are non-biodegradable and toxic in nature [1]. Extensive use of petroleum based lubricants is creating several environmental issues such as surface water and ground water contamination, air pollution, soil contamination, and agricultural product and food contamination [2]. The public awareness for a pollution free environment has resulted in a strict government regulations for petroleum based lubricants and hence, the new technologies are aimed to develop lubricant base oil from renewable sources. Synthetic lubricants, solid lubricants and vegetable oil based lubricants are the alternatives to the petroleum based lubricants, and they are currently being explored by the scientists and tribologists [3].

Vegetable oil based lubricants are highly attractive substitute to the petroleum based lubricants because these are environmentally friendly, renewable, non-toxic and completely biodegradable. Vegetable oil based lubricants are preferred not only because of renewability but also because of their excellent lubricating

properties such as high viscosity index (i.e., minimum changes in viscosity with temperature), high flash-point, low volatility, good contact lubricity, and good solvents for fluid additive [4]. However, vegetable oil based lubricants have some drawbacks such as poor low temperature properties (opacity, precipitation, poor flow ability and/or solidification at relatively moderate temperature), poor oxidative and thermal stability (due to the presence of unsaturation) [5]. However, low temperature properties of vegetable oil based lubricants can be attenuated with the use of additives [4,6]. The oxidative stability of the vegetable oil based lubricants can be improved by selective hydrogenation of polyunsaturated C=C bonds of fatty acid chain [7], or conversion of C=C double bonds to oxirane ring via epoxidation [8,9]. A wide range of reactions can be carried out under moderate reaction conditions by modification of C=C double bonds to oxirane ring [10] and hence, it received more attention as compared to hydrogenation of C=C double bonds. Bio-lubricant obtained from vegetable oils involves three steps: (i) epoxidation of oil to produce epoxy oil, (ii) ring opening of epoxy oil, and (iii) esterification (Fig. 1). Epoxidised vegetable oil is produced industrially by in situ epoxidation process, in which acetic or formic acid reacts with hydrogen peroxide in the presence of mineral acid such as sulfuric or phosphoric acid [11]. However, use of strong mineral acid leads to many side reactions, such as oxirane ring opening to diol, hydroxyesters, dimer formation, and also hydrolysis of oil. Enzymes, resins and heterogeneous catalysts are being used for the epoxidation of oil to overcome the problems connected with the use of mineral acids [12–14].

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Nomenclature

ECO	reactant species – epoxy canola oil
AA	reactant species – acetic anhydride
EP	product species – esterified product
D_{ECO}	diffusion coefficient ECO in AA (m^2/s)
M_{AA}	molecular weight of acetic anhydride
V_{ECO}	molar volume of epoxy canola oil
$k_{c_{ECO}}$	mass transfer co-efficient for epoxy canola oil
W_{ECOR}	mass transfer flux
R_p	particle radius
D_{eECO}	effective diffusivity of epoxy canola oil
(θ)	porosity of the catalyst
K_1	equilibrium constant for adsorption of ECO on catalyst surface (L/mol)
K_2	equilibrium constant for adsorption of AA on catalyst surface (L/mol)
K_{SR}	equilibrium constant for surface reaction (L/mol)
K'_{EP}	equilibrium constant for desorption of EP on catalyst surface (mol/L)
r_{ECO}	observed rate of reaction ($mol/g\ cat.\ h$)
C_t	total active sites
t	time (h)
w	catalyst loading ($g/cat/L$ of liquid phase)
ρ	density of catalyst particle (g/cm^3)
τ	tortuosity
μ	viscosity of reaction mixture ($kg/m/s$)

Goud et al. [15] reported epoxidation of Mahua oil (*Madhumica indica*) by using mineral acid (nitric acid and sulfuric acid) as catalyst, hydrogen peroxide as oxygen donor and acetic acid as an active oxygen carrier. Dinda et al. [16] studied on the kinetics of epoxidation of cotton seed oil by peroxyacetic acid generated in situ from hydrogen peroxide and glacial acetic acid in the presence of mineral acid. Lu et al. [17] reported the epoxidation of soyabean methyl ester by using *Candida Antarctica* lipase immobilized on polyacrylic resin in the presence of hydrogen peroxide and free fatty acid. Orellana-Coca et al. [13] synthesized alkylstearates by using immobilized lipase (*Candida Antarctica* lipase) followed by epoxidation of oleic acid. Most of enzymes resulted in deactivation during epoxidation of oil due to the presence of hydrogen peroxide. Tornvall et al. [18] studied the stability of *Candida Antarctica* lipase B during the chemo-enzymatic epoxidation of fatty acids, and reported that, temperature control and careful dosage of hydrogen peroxide is essential for chemo-enzymatic process. Meshram et al. [19] used acidic cation exchange resin Amberlite IR-122 for epoxidation of wild safflower oil by using hydrogen peroxide and acetic acid. Mungroo et al. [20] used Amberlite IR-120H resin for epoxidation of canola oil using hydrogen peroxide and acetic acid/formic acid, and concluded that acetic acid is a better oxygen carrier as compared to formic acid. Sinadinovic-Fiser et al. [20] studied the kinetic study of epoxidation of soyabean oil in the presence of ion exchange resin, and kinetic parameters were estimated by fitting experimental data using Marquardt method [8].

Limited literature is available on epoxy ring opening of epoxy vegetable oil to esterified product. Hwang and Erhan [6] studied sulfuric acid catalyzed epoxy ring-opening reaction of epoxidized soybean oil with various linear and branched alcohols followed by esterifying the resulting hydroxyl group with an acid anhydride. Adhvaryu et al. [1] prepared dihydroxylated soyabean oil by using perchloric acid, and further esterified with acetic, butyric, hexanoic anhydride in the presence of equimolar quantity of pyridine. Salimon et al. [21] reported three step processes, epoxidation of ricinoleic acid by using hydrogen peroxide and formic acid followed

by ring opening with various fatty acids by using p-toluenesulfonic acid, and finally esterification with 1-octanol using sulfuric acid. So far no literature is available at ring opening of oxidized oil to the esterified product (bio-lubricant) by using heterogeneous catalyst. The heterogeneous catalyst is one of the key steps to achieve the objective of green and sustainable chemistry, hence innovative efforts are made to design of a new catalyst system with higher catalytic activity and stability. Heterogeneous catalyst is preferred over a homogeneous catalyst on the basis of ease of separation, catalyst reuse and environmental safety [22].

Biolubricant is obtained from epoxy oil by two step process: (i) epoxy ring opening, and (ii) esterification reaction. The main objective of the current investigation is to produce high quality biolubricant from canola oil by using a novel sulfated Ti-SBA-15 catalyst. This is for one step reaction (ring opening followed by esterification reaction) of epoxy canola oil to the esterified product (bio-lubricant) (Fig. 1, step-2). Based on our knowledge, this is the first report on one step reaction as well as heterogenous catalyst based process. Another objective is to determine the reaction mechanism, detailed kinetic study to find the order of reaction, and to calculate the apparent activation energy of the reaction. Tribological properties of prepared bio-lubricant were measured by viscosity, cloud point, pour point, oxidative stability, and lubricity testing by high frequency reciprocating rig apparatus.

2. Experimental

2.1. Chemicals and reagents

Canola oil was supplied by Loblaws Inc. (Montreal, Canada). The sources of other chemicals are as follows: glacial acetic acid (100%) from EMD Chemicals Inc. (Darmstadt, Germany), methylene chloride from Sigma-Aldrich (St. Louis, MO, USA), chlorosulfonic acid from Sigma-Aldrich (St. Louis, MO, USA), GR grade hydrogen peroxide (30 wt%) from EMD Chemicals Inc., Amberlite IR-120 from Sigma-Aldrich (St. Louis, MO, USA), ethyl acetate from EMD Chemicals Inc., Wijs' solution were procured from VWR (San Diego, CA, USA), 33% HBr in acetic acid, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), titanium isopropoxide, tetraethyl orthosilicate were obtained from EMD Chemicals Inc.

2.2. Catalyst synthesis

Ti-SBA-15 with different Si/Ti ratios (10, 20, 40, 80) and novel sulfated Ti-SBA-15(10) were prepared according to the method reported by Sharma et al. [23]. The molar gel composition of the solution was TEOS (0.988): $Ti(O^{i}Pr)_4$ (0.024–0.05): P123 (0.016): HCl (0.46): H_2O (127). Ti-SBA-15 with $Si/Ti = 10$ was synthesized by mixing pluronic P123 (9.28 g) in water (228.6 g). The solution was stirred for 2 h at 40 °C. Thereafter, 4.54 g of HCl (37 wt%) was added to the solution and stirred for another 2 h. Then, a mixture of tetraethylorthosilicate (20.83 g) and titanium isopropoxide (2.84 g) was added drop wise, and then the solution was stirred for 24 h at 40 °C. Hydrothermal treatment was done by keeping the solution at 100 °C for 24 h in teflon bottle. The solid material was recovered by filtration, washed with water, and kept at 100 °C for 12 h. Finally, the material was calcined at 550 °C for 6 h. The samples were labeled as Ti-SBA-15(10), where 10 denotes Si/Ti ratio in the material. The same procedure was followed to prepare other materials having different Si/Ti ratios such as 20, 40 and 80 by varying the molar composition of tetraethylorthosilicate and titanium isopropoxide. Sulfation of Ti-SBA-15(10) was carried out using 0.5 M solution of chlorosulfonic acid (in methylene dichloride). Further,

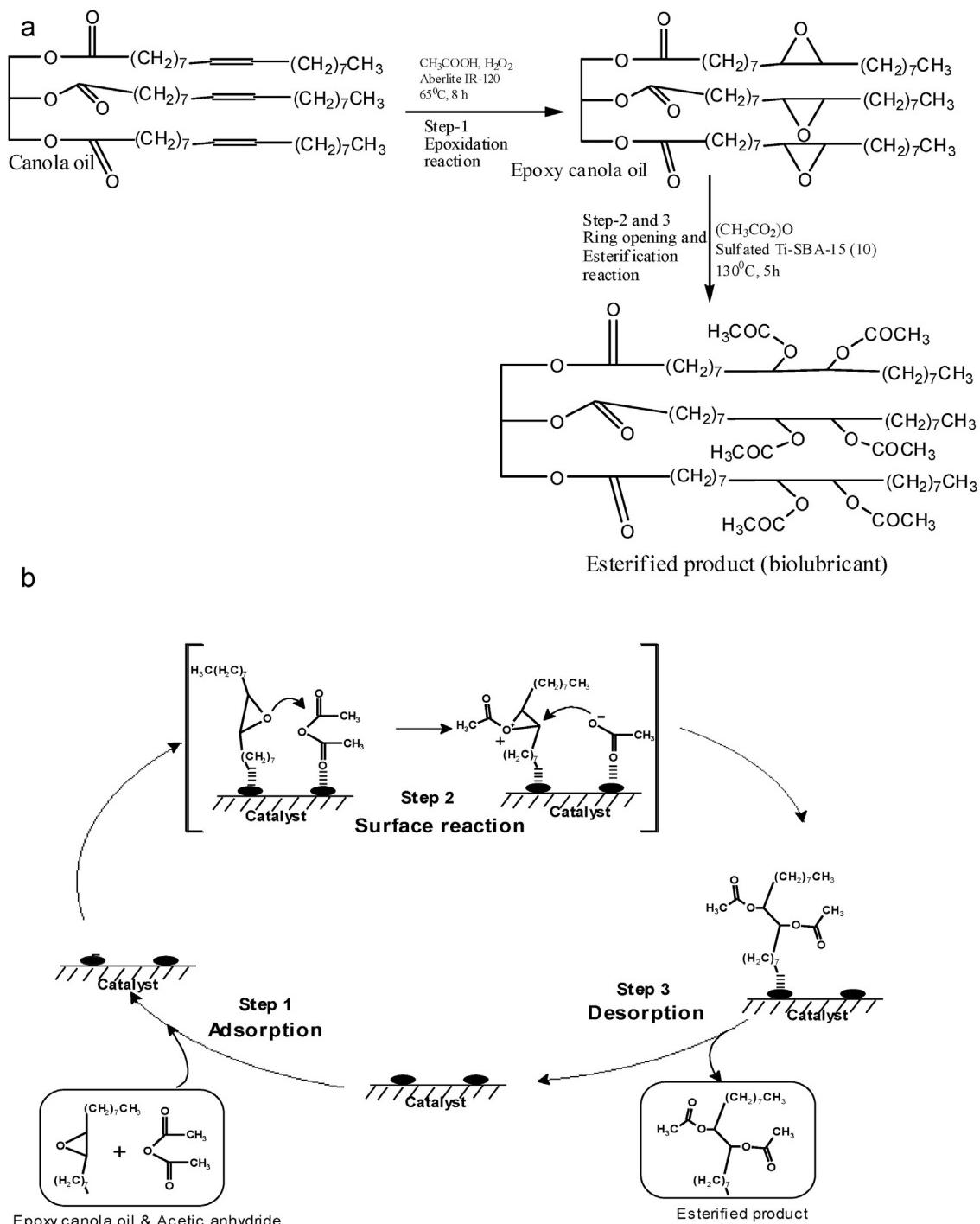


Fig. 1. Reaction scheme and LHHW type reaction mechanism. (a) Reaction scheme for preparation of esterified product (bio-lubricant) from canola oil. (b) LHHW type of reaction mechanism for ring opening of epoxy canola oil to esterified product.

the catalyst was calcined at 550°C for 3 h and denoted as sulfated Ti-SBA-15(10).

2.3. Experimental setup and procedure

2.3.1. Epoxidation of canola oil

Epoxidation of canola oil was carried out in a three necked round bottom flask (500 mL capacity), equipped with overhead stirrer and placed in an oil bath at $65 \pm 2^\circ\text{C}$ of temperature. The side neck of the flask was connected to a reflux condenser, and the thermometer was introduced through another side neck to record

the temperature of the reaction mixture. Epoxidised canola oil was prepared by a method reported in the literature by Mungroo et al. [20]. A 22.6 g of canola oil was placed in the round bottom flask, a calculated amount of acetic acid (acid to ethylenic unsaturation molar ratio, 0.5:1), and Amberlite IR-120 catalyst (22 wt% of oil) were added, and the mixture was stirred continuously for 30 min. Then, 17 g of 30% aqueous H_2O_2 (hydrogen peroxide to ethylenic unsaturation molar ratio 1.5:1) was added. The reaction mixture was continuously stirred for 8 h. The complete conversion of canola oil was monitored by iodine value and oxygen content. Thereafter, the reaction mixture was filtered and extracted with ethyl acetate,

washed with water to remove acetic acid, and then concentrated in rotary evaporator to obtain viscous oil. Epoxidised canola oil was confirmed by FT-IR, ¹H NMR, and ¹³C NMR.

2.3.2. Epoxy ring opening of epoxidised canola oil

Ring opening and esterification reactions were carried out simultaneously in a three necked round bottom flask (100 mL capacity), equipped with a magnetic stirrer and placed in an oil bath. The center neck of the flask was connected to a reflux condenser, and a thermometer was introduced through one of the side necks of flask to record the temperature of the reaction mixture, and oil bath was maintained at the desired temperature of 130 ± 2 °C. Typically, 3.0 g of epoxidised canola oil, 4.5 g of acetic anhydride and 10 wt% of catalyst with respect to epoxy canola oil were placed in the flask and the mixture was continuously stirred for 5 h at 130 °C. Zero time sample was withdrawn before the addition of catalyst and the course of the reaction was monitored by withdrawing the samples at regular intervals. The samples were filtered to remove the catalyst and solution was analyzed for oxirane content.

2.4. Method of analysis

The iodine value was determined using Wijs solution according to the method reported in AOCS Cd 1–25. The oxirane oxygen content of each sample was determined by using the standard AOCS Cd 9–57 method. In this method, samples were titrated with 0.1 N HBr solution (in acetic acid) using crystal violet as an indicator. All experiments were repeated thrice and have ±3% error. The product was confirmed by FTIR, ¹H NMR and ¹³C NMR. Oxirane oxygen content and percentage conversion was calculated as follows:

Oxirane oxygen content

$$= \frac{\text{mL of HBr solution required to titrate sample} \times N \times 1.60}{\text{mass of sample (g)}} \quad (1)$$

where *N* is the normality of the HBr solution.

Conversion (%)

$$= \frac{\text{Oxirane content at time } (t_0) - \text{Oxirane content at time } (t_f)}{\text{(Oxirane content at time } (t_0))} \times 100 \quad (2)$$

2.5. Tribological property of esterified product (bio-lubricant)

The viscosity of the esterified product was measured at 100 °C. The measurements were carried out using a DV-II + Pro Viscometer (Brookfield, USA), equipped with a constant temperature bath. Kinematic viscosity was measured as the method mentioned with ASTM standard D445 – 12. The viscosity measurement was made in duplicate to eliminate error and the average of the two values was reported. Cloud point and pour point temperature was determined in accordance with ASTM standard methods, D2500 – 11 and D97 – 11 respectively, using a K46100 Cloud Point & Pour Point Apparatus (Koehler Instrument Company, Inc., USA). Oxidative stability was determined in accordance with AOCS Cd 12b – 92 standard method, using Metrohm 743 Rancimat® (Metrohm, Canada) equipment at a standard temperature of 110 °C under a continuous flow of air at 15 L/h. The time at which a steady increase in the conductivity value of the conductivity cell was recorded, was denoted as oxidative induction time (OIT). Lubricity testing was carried out using High Frequency Reciprocating Rig (HFFRR) apparatus, according to ASTM D6079 – 04 method. A 0.2 mL of canola oil derived bio-lubricant was added to 1.8 mL of pure diesel fuel. The test sample was placed on sample container which has a smooth metal surface. The ball was placed in contact with the metal surface at 50 Hz for 75 min,

and the wear scar diameter on the ball surface was then measured using a microscope.

3. Results and discussion

3.1. Catalyst characterization

The sulfated Ti-SBA-15(10) catalyst was characterized by FT-IR, X-ray diffraction analysis (XRD), N₂ adsorption–desorption isotherms (specific surface area, mean pore diameter and pore volume), NH₃-temperature programmed desorption analysis (NH₃-TPD) and energy dispersive X-ray analysis (EDX elemental analysis), and reported previously from laboratory by Sharma et al. [23]. A few silent features were reported in this paper. FT-IR spectra of Ti-SBA-15(10) and sulfated Ti-SBA-15(10) show the band at 966 cm⁻¹ is due to Si–O–Ti vibration (Fig. 2a). Ti-SBA-15(10) catalyst absorbs the water molecules after treatment with chlorosulfonic acid, and hence the band at 1716 cm⁻¹ is due to vibration of adsorbed water molecule present in sulfated Ti-SBA-15(10) catalyst [24,25]. The band at 1388 cm⁻¹ in sulfated Ti-SBA-15(10) catalyst is attributed to sulfate group vibration. The band at 800, 1069 and 1228 cm⁻¹ show Si–O bonding present in Ti-SBA-15(10) and sulfated Ti-SBA-15(10) catalysts which agrees with the literature [26,27]. Table 1 represents the BET surface area, pore volume, pore diameter and EDX elemental analysis of Ti-SBA-15 with Si/Ti ratio from 10–80, and sulfated Ti-SBA-15(10). The data has an error of ±2% which confirmed from duplicate analysis. It is observed that chlorosulfonic acid treatment on Ti-SBA-15(10) decreased the specific surface area from 993 to 594 m²/g. It can be due to the formation of sulfate linkage in sulfated Ti-SBA-15(10) catalyst which is also confirmed by FT-IR spectra by the band at 1388 cm⁻¹ due to sulfate group vibration. The specific surface area, mean pore volume and pore diameter of sulfated Ti-SBA-15(10) catalyst were found to be 594 m²/g, 0.99 cm³/g and 6.6 nm, respectively. The EDX data of sulfated Ti-SBA-15(10) catalyst demonstrate that 2.1 wt% of sulfur is present in the catalyst. The XRD patterns of SBA-15, Ti-SBA-15(10) and sulfated Ti-SBA-15(10) are represented in Fig. 2b. The sharp peaks at around 2θ = 0.80 and weak peaks at 2θ = 1.6 and 2.07 are present in all three catalysts which indicate high structure periodicity due to better condensation between silanol and titanium centers [28]. These peaks can be indexed to the 100, 110 and 200 reflections which are characteristic of long range 2D hexagonal order of P6mm symmetry structure, which is in accordance with the literature report [29,30]. Therefore, it can be concluded that sulfation of Ti-SBA-15(10) does not affect the hexagonal symmetry of Ti-SBA-15(10). The wide angle XRD pattern i.e., from 2θ = 0.5–90 (figure is not shown) has no diffraction peak beyond 2θ = 3 in Ti-SBA-15(10) and sulfated Ti-SBA-15(10) which represents the amorphous nature of the pore wall and absence of any extra-framework TiO₂ phase in both the catalysts which is inconsistent with the literature report [28]. The acidic strength of Ti-SBA-15(10) and sulfated Ti-SBA-15(10) were studied by using NH₃-TPD analysis (Fig. 2c). Sulfated Ti-SBA-15(10) shows one broad peak at 220–390 °C in the strong acid strength range. This high temperature desorption of ammonia is due to the presence of strong acidic sites in the catalyst which is generated by the presence of sulfate linkage in the catalyst and confirmed by FT-IR and EDX data.

3.2. Screening of catalysts

Amorphous SiO₂, SBA-15, Ti-SBA-15 with different Si/Ti ratios (10, 20, 40 and 80), sulfated Ti-SBA-15(10) and commercial catalysts such as Amberlyst-15, IRA-200, IRA-400 are evaluated for ring opening of epoxy canola oil to obtain the esterified product (Table 2). The reproducibility of all experimental data was

Table 1

Textural characterization of Ti-SBA-15 and sulfated Ti-SBA-15 with different Si/Ti ratios (10–80).

Sr. no	Catalyst ^a	S_{BET} (m^2/g)	d_p (nm)	V_p (cm^3/g)	EDX elemental analysis (wt%)			
					Si	Ti	O	S
1	Amorphous SiO_2	1011	2.3	0.59	—	—	—	—
2	SBA-15	864	6.4	1.03	—	—	—	—
3	Ti-SBA-15 (10)	993	5.5	1.36	41.3	7.1	51.6	—
4	Ti-SBA-15 (20)	989	5.4	1.36	43.9	3.7	52.4	—
5	Ti-SBA-15 (40)	1030	5.3	1.38	45.3	1.9	52.8	—
6	Ti-SBA-15 (80)	1066	5.5	1.49	46.1	1.0	52.9	—
7	Sulfated Ti-SBA-15 (10)	594	6.6	0.99	39.3	6.3	52.3	2.1

S_{BET} , specific surface area calculated by the BET method; V_p , pore volume determined by nitrogen adsorption at a relative pressure of 0.98; d_p , mesopore diameter corresponding to the maximum of the pore size distribution obtained from the adsorption isotherm by the BJH method.

^a The number in parenthesis denotes Si/Ti ratio in the sample.

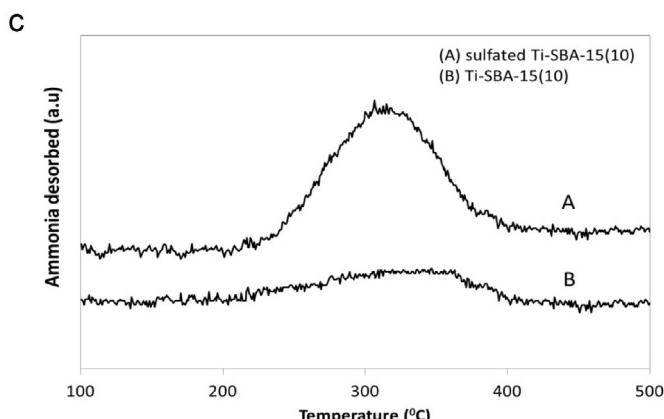
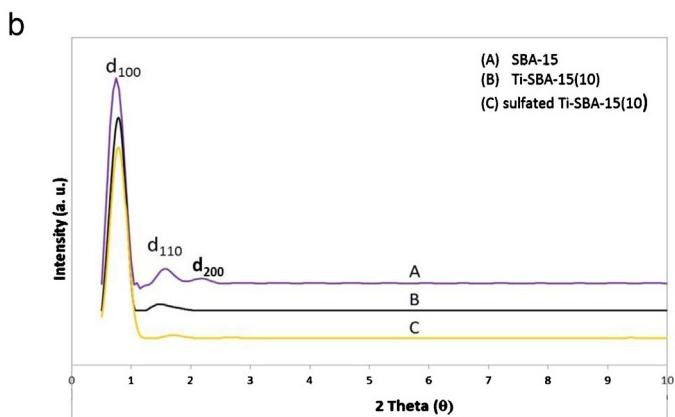
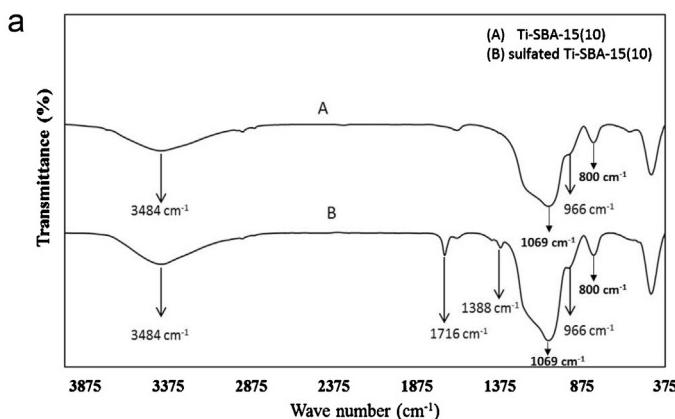


Fig. 2. Catalyst characterization study. (a) FTIR spectra of catalyst. (b) XRD pattern of catalyst. (c) NH_3 -TPD profile of catalyst.

confirmed by performing the reaction in triplicate with an error of $\pm 3\%$. It was reported that with the increase in titanium content in the silica framework increase the acidity of the catalyst [23]. It is found that the percentage conversion increased with increased in titanium content in the catalyst. The sulfated Ti-SBA-15(10) shows the maximum conversion, which is due the presence of a strong acidic center in the catalyst. This strong acidity was confirmed by the NH_3 -TPD profile. Therefore, from above characterization results, it can be concluded that large surface area, mesoporosity and high acidity of sulfated Ti-SBA-15(10) can be responsible for high catalytic activity for ring opening reaction of epoxy canola oil to the esterified product as compared to other commercial catalysts such as Amberlyst-15, IRA-200 and IRA-400. The complete conversion of epoxy ring opening to esterified product is the characteristic of the ideal bio-lubricant [14]. As the unconverted epoxy linkage form free hydroxyl group in the lubricant during fuel combustion inside the engine, and leads to self-polymerization which results into engine coking [35,36]. The novel sulfated Ti-SBA-15(10) resulted into complete conversion of epoxy canola oil hence, used for further reaction optimization.

3.3. Effects of speed of agitation, external mass transfer resistance, and intra-particle diffusion resistance

In any industrial process, the overall rate of the reaction is limited by the rate of mass transfer of reactants between the bulk liquid phase and the catalytic surface. Bio-lubricant is a long chain high molecular weight compound therefore, the effective conversion of an epoxy product to esterified product is much influenced by mass transfer resistance. The liquid surrounding the catalyst particle forms an inter-phase between catalyst surface and liquid phase which causes resistance which is known as external mass transfer resistance. The flow of substrates into the pore to reach the active site of the

Table 2

Effect of various catalysts on % conversion of epoxy canola oil to esterified product.

Sr. no.	Catalysts	Conversion (%)
1	Amorphous SiO_2	5
2	SBA-15	7
3	Ti-SBA-15 (80)	11
4	Ti-SBA-15 (40)	19
5	Ti-SBA-15 (20)	26
6	Ti-SBA-15 (10)	32
7	Sulfated Ti-SBA-15 (10)	100
8	Amberlyst-15	55
9	IRA-400	24
10	IRA-200	19

Reaction conditions: epoxidised canola oil (3.0 g), acetic anhydride (4.5 g), catalyst (10 wt% w.r.t. epoxy canola oil), agitation speed (1000 rpm), temperature (120 °C), time (8 h).

Table 3

Effect of speed of agitation on % conversion of epoxy canola oil to esterified product using sulfated Ti-SBA-15(10) catalyst.

Speed of agitation (rpm)	Conversion (%)
600	85
800	92
1000	100
1200	100

Reaction conditions: Epoxidised canola oil (3.0 g), acetic anhydride (4.5 g), catalyst (10 wt% w.r.t. epoxy canola oil), temperature (130 °C), time (5 h).

catalyst is known as internal mass transfer resistance [32]. The novel sulfated Ti-SBA-15(10) catalyst has uniform mesopore and high surface area which is confirmed by surface area measurement and XRD analysis hence can act as suitable catalyst for such bulky molecular transformation by decreasing both the external and internal mass transfer resistance. The external mass transfer resistance was investigated by carrying out the reaction at 600, 800, 1000 and 1200 rpm. The conversion of epoxy canola oil was found to be 100% at 1000 rpm (Table 3), and beyond 1000 rpm conversion remained constant, indicating that there was no external mass transfer resistance on the overall rate of reaction. Theoretical calculations (shown below) also confirmed the absence of external mass transfer resistance. Thus, the speed of agitation was kept at 1000 rpm for further experiments for the assessment of the effect of other variable parameters on the reaction.

The Wilke–Change equation and Sherwood number were used to calculate internal mass transfer resistance. The internal mass transfer resistance was calculated from the mass transfer coefficient for the reactants, which were obtained from their bulk liquid phase diffusivities. The diffusivity of the limiting reactant (epoxy canola oil) was calculated from the Wilke–Change equation given by $D_{ECO} = 117.3 \times 10^{-18} \times (\psi \times M_{AA})^{0.5} \times T / (\mu \times V_{ECO}^{0.6})$, where $\psi = 1$ (the association factor for acetic anhydride); M_{AA} is molecular weight of acetic anhydride; T , reaction temperature in K; μ is the viscosity of reaction mixture; and V_{ECO} is the molar volume of epoxy canola oil [31]. The value of D_{ECO} calculated to be $8.66 \times 10^{-14} \text{ m}^2/\text{s}$. The value of mass transfer co-efficient for epoxy canola oil k_{ECO} was calculated from Sherwood number $Sh = k_{ECO} \times D_p / D_{ECO}$ and the value was found to be $1.73 \times 10^{-8} \text{ m/s}$. The Sherwood number was taken to be 2 by assuming the extreme case [31]. The mass transfer flux of epoxy canola oil is given by $W_{ECO} = k_{ECO} \times C_{ECOS}$ and the value obtained was $1.10 \times 10^{-7} \text{ mol/m}^2\text{s}$. The initial reaction rate was calculated from standard reaction and found to be $3.26 \times 10^{-8} \text{ mol/m}^2\text{s}$. It confirms that the mass transfer rates were higher than the overall rates of reaction and hence speed of agitation had no influence on reaction rate beyond 1000 rpm. It also ensured that there was no internal mass transfer resistance during the reaction, and all data collected can be used for intrinsic kinetic study.

The influence of intra-particle diffusion resistance was evaluated using Weisz–Prater criterion [32]. The dimensionless parameter $\{C_{WP} = r_{obs} \times R_p^2 / D_{ECO} [C_{ECOS}]\}$ represents the ratio of the intrinsic reaction rate to the intra-particle diffusion rate, can be evaluated from the observed reaction rate, the particle radius (R_p), effective diffusivity of the epoxy canola oil (D_{ECO}) and concentration of the reactant at the external surface particle [C_{ECOS}]. The effective diffusivity of epoxy canola oil (D_{eECO}) inside the pores of the catalyst was calculated to be $9.18 \times 10^{-16} \text{ m}^2/\text{s}$ from bulk diffusivity D_{ECO} , porosity (θ) and tortuosity (τ). The average values of porosity and tortuosity were taken as 0.4 and 3, respectively. In the present case, the highest value of C_{WP} was calculated as 0.45, which is less than 1. Hence, intra particle mass transfer resistance is absent for this reaction [32]. Hence, we can conclude that 1000 rpm is sufficient for complete conversion of the epoxy product to esterified product which is required for ideal bio-lubricant.

3.4. Effect of acetic anhydride

The ring opening of epoxy canola oil to produce esterified product was carried out by acetic anhydride. It was mentioned in the literature that esterification with acetic anhydride leads to high quality lubricant [1,6]. Acetic anhydride produces di-acetylated product while acetic acid resulted into the mono acetylated product. Hence, acetic anhydride was selected in the present study. Martini et al. [33] used different cyclic dicarboxylic anhydride for ring opening reaction. Lathi et al. [14] used acetic anhydride for esterification reaction, and reported that the prepared biolubricant has better lubricating property. In this study, the amount of acetic anhydride was increased in the reaction from 1.5 to 4 wt% of epoxy canola oil (Fig. 3a). It was found that with an increase in the amount of acetic anhydride, the conversion to esterified product (biolubricant) decreases which also resulted into the biolubricant with more epoxy linkage. This decrease can be due to adsorption of acetic anhydride on the catalyst's active sites, which is an agreement with the literature reported by Dejaegere et al. [34]. It is reported that the presence of two acyl groups on acetic anhydride increases the driving force for adsorption of acetic anhydride on the catalyst. It was also observed that with acetic anhydride less than 1.5 wt%, the reaction becomes viscous in nature, and it was difficult to separate the catalyst from the reaction. Therefore, further reaction optimization was carried out by using 1.5 wt% of acetic anhydride to obtain bio-lubricant with complete conversion of epoxy product to esterified product.

3.5. Effect of catalyst loading and temperature

The effect of catalyst loading on the reaction was evaluated by varying the catalyst loading in 5–20 wt% with respect to epoxy canola oil. It was observed that the percentage conversion of epoxy canola oil was increased with catalyst loading (Fig. 3b), which was due to the proportional increase in the active site of the catalyst. Fig. 4a shows that the initial rate of the reaction was increased linearly with increase in catalyst loading in the reaction from 5 to 20 wt%. It was also investigated that in the absence of catalyst, the reaction did not proceed. The highest conversion of epoxy canola oil was observed with catalyst loading of 10, 15 and 20 wt%. The reaction with catalyst loading of 15 and 20 wt% was found to be faster as compared to that with 10 wt% of loading. However, in case of kinetic study a slow reaction is more preferred over the fast reaction; therefore further studies were carried out with 10 wt% of catalyst loading to obtain the bio-lubricant with complete conversion of epoxy product to esterified product.

The reactions were carried out using sulfated Ti-SBA-15(10) catalyst with a temperature range 100–130 °C using catalyst loading of 10 wt% to investigate its effects on conversion of the epoxy ring opening of canola oil to esterified product. During the experiments the samples were collected periodically, and oxirane content was analyzed to calculate % conversion of epoxy canola oil. It was found that with an increase in the temperature, the conversion of epoxy canola oil was also increased (Fig. 3c). The reaction mixture became viscous and dark in appearance at 140 °C, which can be due to the polymerization reaction, that initiated at the reflux temperature of acetic anhydride. Park et al. [35,36] also investigated that epoxy oil is susceptible to the polymerization reaction at higher temperature. Hence, ideal bio-lubricant can be obtained at 130 °C. At 130 °C of temperature no polymerization of bio-lubricant was observed which is also confirmed by FTIR, NMR and molecular weight analysis results (described in Section 3.8). A 100% conversion of epoxy canola oil to esterified product was obtained at 130 °C; hence, this temperature was chosen for further experiments to obtain ideal biolubricant.

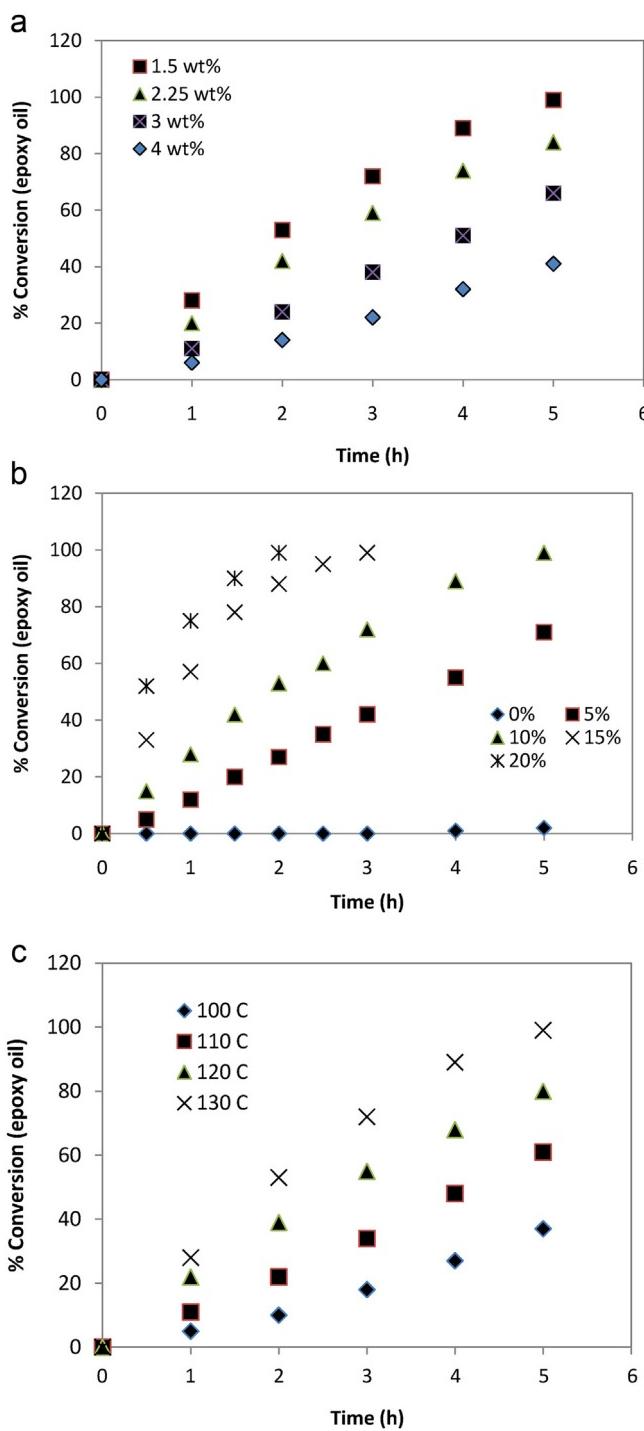


Fig. 3. Reaction parameter optimization study for conversion of epoxy canola oil to esterified product. Reaction conditions: Epoxidised canola oil (3.0 g), acetic anhydride (1.5–4.0 wt%), catalyst (0–20 wt% w.r.t. epoxy canola oil), agitation speed (1000 rpm), temperature (110–130 °C), time (5 h). (a) Effect of acetic anhydride. (b) Effect of catalyst loading. (c) Effect of temperature.

3.6. Catalyst reusability study

Catalyst reusability is an important criteria for green and sustainable technology. The reusability of sulfated Ti-SBA-15(10) catalyst was carried out up to four runs (Table 4). After each run, catalyst was filtered and refluxed with 100 mL of acetone to remove the reactant and product adsorbed on the catalyst surface. Further, the catalyst was dried at 120 ± 10 °C for 3 h. In a batch reaction,

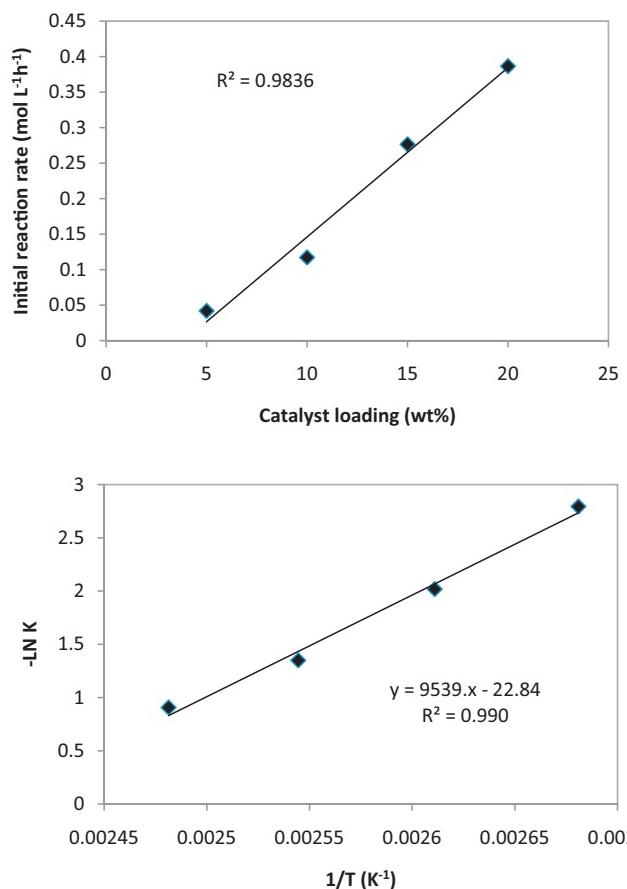


Fig. 4. Kinetic study for conversion of epoxy canola oil to esterified product. Reaction conditions: Epoxidised canola oil (3.0 g), acetic anhydride (1.5 wt%), catalyst (10 wt% w.r.t. epoxy canola oil), agitation speed (1000 rpm), temperature (110–130 °C), time (5 h). (a) Plot of initial reaction rate vs. catalyst loading. (b) Arrhenius plot ($-\ln k$ vs. $1/T$).

there was an inevitable loss of particles during filtration and handling. Hence, the actual amount of catalyst used in the next batch, was almost 5% less than the previous batch. The loss of the catalyst was made up with fresh catalyst. The marginal decrease in the conversion of epoxy canola oil to esterified product was observed after each run. Hence, it can be concluded that the catalyst has good reusability.

3.7. Development of kinetic model and reaction mechanism for the ring opening of epoxy canola oil to esterified product

The plausible mechanistic pathway of ring opening of epoxy canola oil to esterified product can be predicted by development of kinetic model. For this study, reactions were carried out at 100, 110, 120 and 130 °C and samples were analyzed periodically to develop the kinetic model of the reaction (Fig. 3c). Eley–Rideal and

Table 4

Reusability study of sulfated Ti-SBA-15(10) catalyst on % conversion of epoxy canola oil to esterified product.

Catalyst run	Conversion (%)
1st	99
2nd	96
3rd	92
4th	87

Reaction conditions: Epoxidised canola oil (3.0 g), acetic anhydride (4.5 g), catalyst (10 wt% w.r.t. epoxy canola oil), agitation speed (100 rpm), temperature (130 °C), time (5 h).

Langmuir–Hinshelwood–Hougen–Watson (LHHW) type mechanism were tested, and LHHW type mechanism was found to hold good for ring opening of epoxy canola oil to esterified product. LHHW type mechanism proceeds via involvement of two sites (similar in nature) and the reaction was controlled by 3 steps, viz., adsorption, surface reaction and desorption. It was assumed that epoxy canola oil (*ECO*) and acetic anhydride (*AA*) were weakly adsorbed on the catalyst active sites. Adsorption of *ECO* on vacant site is given by,



Adsorption of *AA* on vacant site is given by



Surface reaction of *ECO* and *AA* form esterified product (*EP*) on the site.



Desorption of esterified product is given by



Surface reaction is the rate controlling reaction, and then the rate of reaction of *ECO* is given by

$$-r_{ECO} = -\frac{dc_{ECO}}{dt} + K_{SR}C_{ECO.S} \cdot C_{AA.S} - K'_{SR}C_{EP.S} \cdot C_S \quad (7)$$

Value of *C_s* can be calculated from site balance,

$$C_t = C_{ECO} + C_{AA} + C_{EP} + C_S \quad (8)$$

where *C_t* = Total active sites available.

$$-\frac{dc_{ECO}}{dt} = \frac{K_{SR}C_t^2 \{K_1K_2C_{ECO} \cdot C_{AA} - (k'_{SR}C_{ECO}/k_{SR})\}}{(1 + K_1C_{ECO} + K_2C_{AA} + C_{EP}/K_{EP})^2} \quad (9)$$

When the reaction is far away from equilibrium,

$$-\frac{dc_{ECO}}{dt} = \frac{k_r w C_{ECO} \cdot C_{AA}}{(1 + K_1C_{ECO} + K_2C_{AA})^2} \quad (10)$$

At time (*t*) = 0, *C_{EP}* = 0

$$-\frac{dc_{ECO}}{dt} = \frac{k_r w C_{ECO} \cdot C_{AA}}{(1 + K_1C_{ECO} + K_2C_{AA})^2} \quad (11)$$

where *k_rw* = *K_{SR}K₁K₂C_t²*; *w* = catalyst wt (g cat/L of liquid phase). If the adsorption constants are very small, then the above equation reduces to

$$-\frac{dc_{ECO}}{dt} = k_r w C_{ECO} \cdot C_{AA} \quad (12)$$

A large excess of acetic anhydride was used in the reaction. Therefore, *C_{AA}* ≈ *C_{AA,0}* can be assumed in this reaction. Hence, the above equation can be written in term of fractional conversion as,

$$\frac{dX_{ECO}}{dt} = k'(1 - X_{ECO}) \quad (13)$$

where

$$k' = k_r w C_{AA,0} \quad (14)$$

Integrating the above equation, the final expression leads to

$$-\ln(1 - X_{ECO}) = k't \quad (15)$$

Thus, a plot of $-\ln(1 - X_{ECO})$ against time (*t*) was made for at different temperatures. It resulted in different reaction rate constants at different temperatures (Table 5). From the kinetic model data, it was observed that the reaction rate constant increases with an increase in the temperature, indicating that the reaction is endothermic, and the reaction is a pseudo first order with respect

to epoxy canola oil. Arrhenius plot was made by plotting $-\ln k$ vs. $1/T$ (Fig. 4b). The value of apparent activation energy of epoxy ring opening of epoxy oil to esterified product was found to be 19.0 kcal/mol. This value confirms that the reaction is kinetically controlled.

The exact reaction pathway for ring opening of epoxy canola oil to epoxidised product by heterogeneous catalyst is not fully understood. However, Laitinen et al. [37] reported the mechanism of acid catalyzed epoxide ring opening of methyloxirane which is based on Ab initio quantum mechanical and density functional theory calculation. On the basis of above derived LHHW type kinetic model and mechanism reported by Laitinen et al. [37], the plausible LHHW type reaction mechanism is depicted in Fig. 1b. The first step is adsorption, wherein the epoxy canola oil and acetic anhydride are adsorbed on the active sites of the catalyst. The second step is surface reaction, wherein acetic anhydride undergoes a nucleophilic attack by oxygen atom of epoxy ring which resulted in a mono acylated intermediate product and acetate anion. Eventually, the mono acylated intermediate product undergoes a nucleophilic attack by acetate anion to produce diacylated (esterified) product. In the third step, diacylated product is desorbed from the catalyst, and active sites are again regenerated for the next reaction.

3.8. Products isolation, confirmation and their tribological properties

The epoxy canola oil underwent simultaneous ring opening and esterification reactions in the presence of acetic anhydride by sulfated Ti-SBA-15(10) catalyst to produce an esterified product (Fig. 1a, step-2). The progress of the reaction was monitored by oxirane content value, and after complete conversion of epoxy canola oil to esterified product, 100 mL of ethyl acetate was added to the reaction mixture. Thereafter, the catalyst was filtered from the reaction mixture through filter paper. Then, 100 mL of water was added to the filtrate and stirred for 15 min. Ethyl acetate layer was separated through separating funnel and evaporated on rotary evaporator. Viscous yellow colored oil was obtained. The esterified product was confirmed by FTIR, ¹H NMR, and ¹³C NMR.

FT-IR spectra of canola oil (A), epoxy canola oil (B), and esterified product (C) are shown in Fig. 5a. Canola oil (A) has a characteristic band at 3007 cm⁻¹ and 738 cm⁻¹ which is attributed to the C—H stretching and C—H bending of C=C—H double bond. The bands at 3007 cm⁻¹ and 738 cm⁻¹ disappeared after the epoxidation reaction, indicating that almost all —C=C— bonds have been converted into the epoxide. The new band appeared at 831 cm⁻¹ which is attributed to the epoxy group of epoxy canola oil and is in accordance with the literature reported by Vlcek and Petrovic [38]. The FT-IR spectra of the esterified product (C) has no band at 831 cm⁻¹ which is characteristic of epoxy group. The intensity of band at 1750 cm⁻¹ increased, which confirmed the formation of esterified product. Fig. 5b represents ¹H NMR of canola oil (A), epoxy canola oil (B), esterified product (C) and D₂O exchanged esterified product (D). ¹H NMR spectra of epoxy canola oil (B) show the chemical shift of 2.7–3.1 ppm region, which represents both CH—proton attached to the oxygen atom of epoxy group and it is in accordance with the literature report [20]. ¹H NMR spectra of esterified product (C) shows the new chemical shift at 5.0 ppm. This represents CH—proton attached to carbonyl group, while the chemical shift present in 2.7–3.1 ppm in epoxy canola oil (B) is not present esterified product (C) confirming the product formation. The D₂O exchanged ¹H NMR spectra of esterified product (D) confirmed that there is no free hydroxyl group is present in the molecule. The triglyceride backbone is important for maintaining the biodegradability of the vegetable oil [14]. The methane proton of —CH₂—CH—CH₂— glycerol's backbone was also confirmed by the presence of chemical shift in 5.2–5.4 ppm. Fig. 5c represents the ¹³C NMR spectra of canola oil (A),

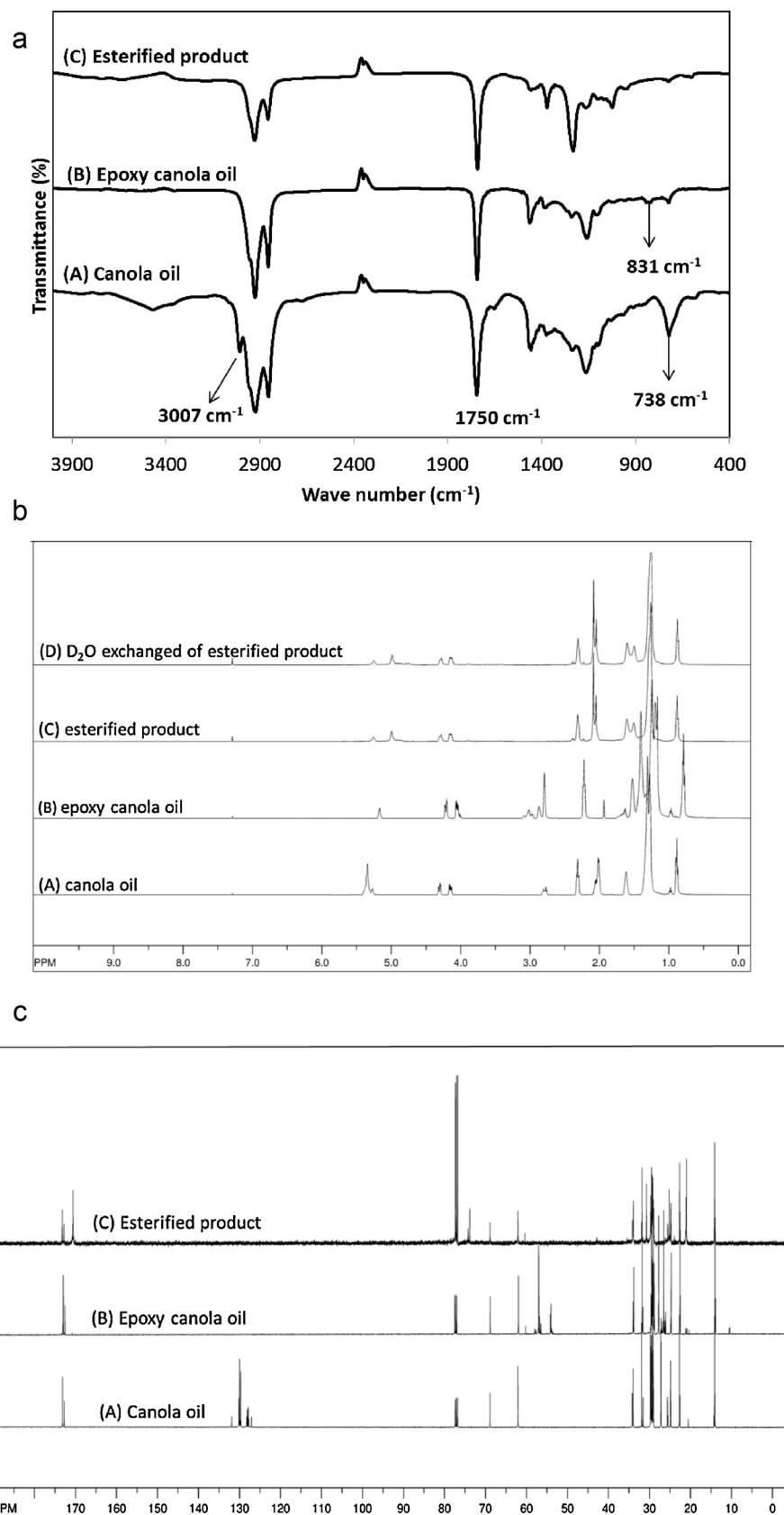


Fig. 5. Product confirmation study. (a) Product confirmation by FTIR spectra. (b) Product confirmation by ^1H NMR spectra. (c) Product confirmation by ^{13}C NMR spectra of product.

Table 5

Rate constant (k) for ring opening of epoxy canola oil to esterified product using sulfated Ti-SBA-15(10) at different temperatures.

Sr. no.	Temperature (°C)	T (Kelvin)	rate constant k , (min $^{-1}$)	$1/T$ (Kelvin $^{-1}$)	$\ln k$
1	100	373	0.0612	0.002681	-2.793
2	110	383	0.1329	0.002611	-2.018
3	120	393	0.2595	0.002545	-1.348
4	130	403	0.4041	0.002481	-0.906

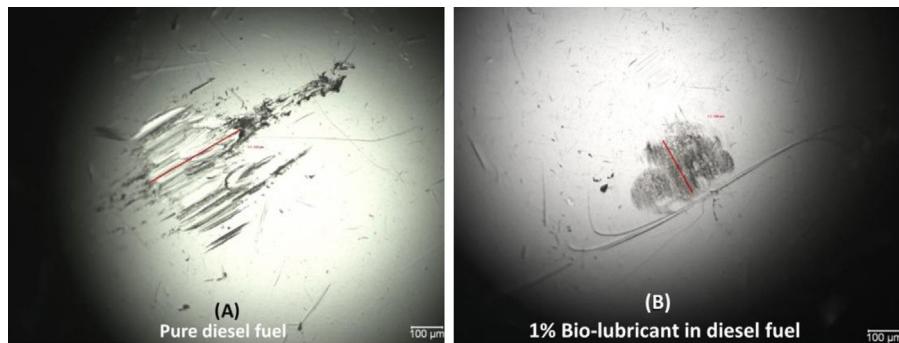


Fig. 6. Microscopic wear scar image on test metal surface.

epoxy canola oil (B) and esterified product (C). The ^{13}C NMR spectra of canola oil (A) shows the signal between 120–140 ppm, which is characteristic of olefinic ($-\text{C}=\text{C}-$) carbon atom. The ^{13}C NMR spectra of epoxy canola oil (B) have no signal between 120–140 ppm, which indicates the complete disappearance of the olefinic carbon ($-\text{C}=\text{C}-$) atom. Also, epoxy canola oil (B) shows signals between 53 and 58 ppm, which is characteristic of the epoxy carbon atom. The ^{13}C NMR spectrum of esterified product (C) shows no signal between 53 and 58 ppm, while new signal at 170 ppm is observed; which is due to the presence of carbonyl carbon atom in the molecule. The molecular weight of the esterified product was found to be 1129 by mass spectrum data which is expected molecular weight, and also confirmed the absence of polymerization of bio-lubricant. Therefore, FT-IR, ^1H NMR, ^{13}C NMR, and mass spectrum confirmed the formation of esterified product in the reaction.

The efficiency of lubricant depends on the viscosity of the liquid to lubricate the contact surfaces of metal. Canola oil derived bio-lubricant was found to be highly viscous. The viscous nature of the product is the result of epoxidation and esterification reaction, which not only removed the unsaturation but also increased the aliphatic linkage in the oil (Fig. 1a). Tribological properties of canola oil derived bio-lubricant are presented in Table 6. The kinematic viscosity of canola oil derived bio-lubricant was measured at 100 °C and was 670 cSt. Oxidative stability is an important property of lubricant because automobile applications are dependent on it. Oxidative stability of canola oil and canola oil derived bio-lubricant was measured, bearing in mind that canola oil has high amount of monounsaturation and polyunsaturation. As a result, the oxidative induction time (OIT) of canola oil and canola oil derived bio-lubricant was found to be 0.6 h and 56.1 h, respectively. The high OIT of canola oil derived bio-lubricant is due to the absence of unsaturation in the bio-lubricant. Cloud point is the temperature at which liquid becomes cloudy in appearance whereas pour point is

the lowest temperature at which it loses flow characteristics. Cloud point and pour point values of canola oil derived bio-lubricant was found to be -3 and -9 °C, respectively. The lubricating property of liquid is defined as the quality that prevents the wear when two moving parts come into contact with each other [39]. ASTM D6079-04 method was used to evaluate lubricating property of bio-lubricant by using the high-frequency reciprocating rig (HFFR) apparatus. Fig. 6 shows the microscopic images of the wear scar generated on test metal surface in the presence of pure diesel fuel and 1% bio-lubricant blended in the diesel fuel. Bio-lubricant blended in the diesel fuel resulted in wear scar of 130 μm , while pure diesel fuel resulted in wear scar of 600 μm . Therefore, it can be concluded that canola oil derived bio-lubricant has good lubricating properties and has a future perspective in automobile industries.

4. Conclusions

Sulfated Ti-SBA-15(10) was found to be the most active, selective, stable and reusable catalyst as compared to other commercial catalysts such as, Amberlyst-15, IRA-200 and IRA-400. A kinetic model for ring opening of epoxy canola oil to esterified product (biolubricant) was developed and it follows the LHHW type mechanism. The oxidative property of bio-lubricant was found to be outstanding due to the absence of unsaturation in molecules. Bio-lubricant also demonstrated excellent lubricity property. Bio-lubricant derived from canola oil is renewable, biodegradable and non-toxic, therefore it can be considered as a replacement for synthetic lubricants.

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Table 6

Tribological properties of esterified product (bio-lubricant).

Sr. no.	Tribological property	Bio-lubricant
1	Viscosity at 100 °C (cSt)	670
2	Cloud point (°C)	-3
3	Pour point (°C)	-9
4	Oxidative induction time (h)	56.1
5	Wear scar diameter (μm)	130

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